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SILVER TRANSPORT IN H-451 GRAPHITE[*]

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Introduction

Diffusion profiles have been measured for silver in hollow and solid cylinders in the temperature range 490°C to 800°C. The profiles show two components of diffusion. There is a high concentration, relatively immobile zone near the surface and a low concentration, rapidly moving component deeper into the sample. The rapid component is well fitted by the diffusion equation when irreversible trapping is assumed. The diffusion coefficients determined by least-square analysis of the profiles can be represented by $D\ (m^2/sec) = 17.4 \exp(-22{,}100/T)$. Excessive scatter was seen in the trapping coefficients determined from the profiles. This is believed to be due to varying amounts of impurities in the different samples. A limited number of desorption measurements were performed for silver from H-451 graphite. Evidence of Elovich-type behavior was noted.

Experimental Procedures

Materials. Great Lakes grade H-451 graphite is a fairly isotropic material which is the reference core graphite for future HTGR's. It is produced by the extrusion of a hot mix of coke particles and pitch binder, baked, impregnated, and graphitized to 2800°C. It is characterized by particles sized up to 1 1/2 mm diam with interconnected pores up to 10 μm in diameter. The samples used in this study had densities varying between 1.73 and 1.77 g/cm^3.

Hollow Cylinder Diffusion Experiments. Some of the diffusion experiments were performed with hollow graphite cylinders with graphite end caps. The lower temperature runs used cylinders with an outer diameter of 1.27 cm, inner diameter of 0.318 cm, and a length of 2.54 cm. For the higher temperature experiments, cylinders with an outer diameter of 5.08 cm, inner diameter of 0.64 cm, and a length of 10.16 cm were used.

The silver nitrate solution was not placed directly on the sample but was applied to either powdered graphite or flexible graphite foils. The solution dried very quickly, leaving silver nitrate on the graphite. After a short anneal at 600°C to dissociate the silver nitrate, the silver-laden graphite was placed inside the cylindrical graphite sample and sealed. The sample was then placed in the annealing system. This system allowed the isothermal anneal to be performed in a vacuum, helium atmosphere, or hydrogen and helium atmosphere. After the isothermal anneal, the end cap was taken off and the silver source removed., The sample was ultrasonically cleaned again to help remove all remaining source contamination. The center of the cylinder was then filled with epoxy to allow the sample to be sectioned all the way down to the inner radius for determination of the radical concentration profile.

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Solid Cylinder Diffusion Experiments. Because of the inaccuracy in measuring the thickness of the last section of the hollow cylinders (the one with the greatest silver concentration), a changeover to solid cylinders was made. The silver was not placed directly on the samples but on flexible graphite foils. The process of silver nitrate dissociation was was identical to that used for the hollow cylinders. The foils were wrapped around the samples and secured in place by wires.

Diffusion of Silver Chloride in Graphite. The procedures for these experiments were similar to those listed for silver diffusion with the exception of the source preparation.

Silver Desorption from H-451 Graphite. Silver (^{110m}Ag) nitrate was deposited uniformly on thin graphite disks and dissociated a short time at 600°C. Because in situ monitoring of the samples was not possible, the desorption anneals were performed in short time steps. At the end of each time interval, the samples were removed and gamma counted in a sodium iodide detector system. This allowed the measurement of silver remaining on the samples as a function of annealing time.

Results and Discussion

Diffusion profiles for silver in H-451 graphite were measured over the temperature range 490°C to 800°C. Maximum silver concentrations were varied over the range of 10 ng/g to 1 μg/g. Early experiments compared the diffusion along and across the axis of extrusion, and no difference was seen. After this, all experiments were performed with diffusion across the axis.

Two features are apparent for all the diffusion profiles. There is a high concentration, slow or non-moving component near the surface. Away from the surface, there is a low concentration, faster moving component. This behavior is similar to results seen for cesium diffusion in graphite.

The silver component near the surface appears to be trapped on active sites created by the sample machining. These active sites are likely a combination of broken crystallites and machining powder left on or near the surface. A decrease in the fraction of the silver appearing in the surface component was seen when the sample surface was cleaned, but it was not possible to lower the fraction to zero.

A simple explanation was sought for the reason that some silver is trapped but some is not. The effect of impurities was considered first. The only silver compounds that are stable at the temperatures where diffusion experiments were performed are the silver halides. The possibility that the mobile component was composed of silver chloride seemed to be a reasonable hypothesis. Motivating this hypothesis, it was noted that silver chloride has a higher vapor pressure than elemental silver and that sufficient chlorine impurity exists in grade H-451 graphite to convert all the diffusing silver to silver chloride. The first experiments performed to test the silver chloride hypothesis involved the exposure of the graphite sample to iodine prior to the silver loading and diffusion anneal. There was a definite increase in the silver in the mobile component due to the iodine exposure. This appeared to provide support for the proposed model. However, as a more direct verification of this model, measurements were made for the rate of silver chloride diffusion in H-451 graphite. It was observed that most of the silver chloride was trapped at the active surface region, even more than was seen for silver diffusion. This would seem to rule out the possibility that the fast diffusion component is the result of silver chloride formation in the graphite. This does not mean that impurity effects are not important in the diffusion of silver in graphite. The experimental results for the samples exposed to iodine prior to the diffusion anneal suggest that impurities can occupy the active sites and allow the silver to bypass the active surface region. In the experiments for silver chloride diffusion, the results show that having the silver in the form of silver chloride does not make it immune to trapping.

Conclusions

(1) Silver diffusion profiles in H-451 graphite show two different components of diffusion. The slower or non-moving component is likely due to adsorption on active sites on or near the surface. (2) The fast component of the diffusion appears to occur along pore surface. This fast component of the diffusion profiles is well fitted by the diffusion equation when irreversible trapping is included. (3) The diffusion coefficient for the fast component varies with temperature as $D(T) = D_0 \exp(-Q/RT)$, with $D_0 = 17.4\ m^2/sec$ and $Q = 183.6$ kJ/mol. (4) The trapping coefficients determined by least-square analysis of the diffusion profiles showed a large amount of scatter. This is thought to be due to variability in the amounts of impurities in each sample. (5) The desorption of silver from H-451 graphite demonstrates an Elovich-type behavior with the concentration of silver remaining on the sample decreasing linearly with the logarithm of time.